Journal of Electroanalytical Chemistry 663 (2011) 48–51

Contents lists available at SciVerse ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Short Communication

Cyclic-voltammetry characteristics of poly(vinyl pyrrolidone) (PVP) on single-crystal Pt surfaces in aqueous H_2SO_4

Luiz H.S. Gasparotto *, Janaina F. Gomes, Germano Tremiliosi-Filho

Instituto de Química de São Carlos, Universidade de São Paulo, 13560-970 São Carlos, São Paulo, Brazil

ARTICLE INFO

Article history:
Received 7 July 2011
Received in revised form 13 September 2011
Accepted 27 September 2011
Available online 4 October 2011

Keywords:
Pt single crystal
PVP
Oxidation
Acid solution

ABSTRACT

In the present paper we investigated the electrochemical behavior of PVP on polycrystalline and single-crystal Pt electrodes. PVP hampered the characteristic hydrogen UPD and anion adsorption on all investigated surfaces. Several oxidation processes appeared in the anodic sweep with Pt(111) and Pt(100) being the most active for the oxidation processes. Repetitive cycling of the PVP_{ads}-modified Pt(111) or Pt(100) electrodes in PVP-free aqueous H_2SO_4 solution leads to a continuous suppression of the characteristic hydrogen UPD and anion adsorption as a consequence of PVP oxidation. However no PVP oxidation was observed when cycling the PVP_{ads}-modified Pt(110) electrode in PVP-free aqueous H_2SO_4 solution.

1. Introduction

A variety of chemical compounds, including poly(vinyl pyrrolidone) (PVP), have been employed as protective agents in the production of nanoparticles. PVP is a homopolymer composed of monomers having a hydrophilic cyclic amide group. The nitrogen and oxygen atoms of this polar group present a strong affinity for gold, silver, platinum ions and their metallic clusters. Therefore PVP is widely employed for nanoparticle fabrication [1–4], since it acts concomitantly as coordinating agent for metallic ions and stabilizing agent for metallic nanoparticles. It is agreed that the general mechanism of protection [1,5–7] involves a lone electron pair donation of —C=O from PVP to the metals and aggregation avoidance through steric effect. Although this mechanism is accepted, the literature completely lacks information on the interaction between PVP and metallic surfaces. It is well known that the adsorption is not only affected by the electronic properties of the surface but also by its structure (crystallographic orientation). We have recently shown [8] that poly(vinyl alcohol) (PVA) interacts differently with distinct single crystal Pt structures and suffers oxidation to some extent. As another example, DeBlois et al. [9] showed, by using platinum electrodes with different orientations, that the bond between adsorbed benzene and Pt(100) is stronger than that between adsorbed benzene and Pt(110) or Pt(111). The understanding of molecular adsorption at well-ordered single crystal surfaces may enable, in principle, the production of preferentially oriented nanoparticles [10].

In this work we studied the electrochemical behavior of PVP at well-ordered single crystal as well as polycrystalline Pt surfaces in H_2SO_4 solution. We discuss the influence of PVP on the hydrogen UPD and anion adsorption on oriented Pt surfaces. Moreover, it is shown that PVP not only behaves distinctly on different oriented surfaces, but also suffers oxidation to some extent.

2. Experimental

The polycrystalline Pt and the single crystals, Pt(111), Pt(110) and Pt(100), disks (10 mm in diameter and 2 mm thick) were purchased from MaTeck and polished to a mirror-like finish with 0.05 μm alumina. Before each experiment, the electrode surface was treated in the following way: the working electrode was flame annealed in a hydrogen flame for 2 min, cooled down to room temperature under Ar + H_2 atmosphere and then protected with a drop of water in equilibrium with this gas mixture to avoid contamination. The electrode was then quickly inserted into the electrochemical cell and a meniscus was formed with the deaerated 0.1 M H_2SO_4 (prepared with 18.2 MΩ cm Milipore/Milli-Q water and Alfa Aesar sulfuric acid). The quality of the surfaces and the cleanness of the system were checked by comparison with the typical voltammograms published by Clavilier [11]. Solutions containing 1% w/w PVP (Aldrich Co; MW: ~10,000) were prepared adding appropriate amounts of PVP into the electrochemical cell. The working electrodes were introduced at 0.05 V *vs* RHE in the electrochemical cell to avoid PVP oxidation.

* Corresponding author. Tel.: +55 16 3373 9934.
E-mail address: lhgasparotto@iqsc.usp.br (L.H.S. Gasparotto).

1572-6657 © 2011 Elsevier B.V. Open access under the Elsevier OA license.
doi:10.1016/j.jelechem.2011.09.025

The counter electrode was a 1 cm × 1 cm platinum sheet. The reference electrode was the reversible hydrogen electrode (RHE) and all potentials in this work are referred to it. The experiments were carried out with a 1285 Solartron potentiostat/galvanostat controlled by the CoreWare software.

3. Results and discussion

3.1. PVP cyclic voltammetry behavior on polycrystalline Pt

Fig. 1 displays cyclic voltammograms (CVs) profiles obtained at 50 mV s^{-1} in the 0.05–1.5 V potential range for the polycrystalline Pt in O_2-free 0.1 M aqueous H_2SO_4 solution with and without 1% w/w PVP. The CV recorded in the PVP-free solution depicted the typical response of polycrystalline Pt, with hydrogen adsorption/desorption processes in the 0.07–0.3 V potential range and the platinum oxides formation (around 1.0 V) and reduction (0.76 V) peaks in acid media. Upon PVP addition and sweeping the potential from 0.05 V to the positive direction, the first CV cycle (red[1] line) shows that both hydrogen-desorption peaks were partially inhibited and slightly shifted towards more positive potentials. The integrated anodic component of the CV obtained in the 0.05–0.35 V range in the PVP-free electrolyte was 214 μC cm^{-2}, while a significantly lower value of 60 μC cm^{-2} was obtained in the PVP-containing solution in the first CV cycle. This result evidences that PVP is already adsorbed on Pt at potentials just positive to the hydrogen evolution. An oxidation wave centered at about 0.62 V can be observed as the sweep continues, followed by a very small shoulder at 0.84 V. Later it will be shown that these oxidation processes are much more evident on Pt(1 1 1) and Pt(1 0 0) and may be ascribed to PVP oxidation. Hassouna et al. [12] showed that the PVP photooxidation generates several intermediates, like succinimide and N-vinylpyrrolidone. Our results show that PVP is subjected to electrochemical oxidation. It is reasonable to assume that different intermediates are formed and could, in turn, adsorb on the Pt surface and be further oxidized (note that at more positive potentials the increasing current does not cease). We performed *in situ* FTIR spectroscopy experiments in the thin-layer configuration to probe PVP oxidation products formed, however no substantial differences appeared in the interferograms upon potential modulation. As the contribution of solution species to the FTIR signal is much larger than the contribution of adsorbed ones the FTIR technique is usually not able to probe only interfacial changes [13]. Sum frequency generation (SFG) spectroscopy is a much more appropriated technique because it is intrinsically sensitive to the interface response. SFG experiments are already in course in our laboratory and will be presented in a future paper. During the back scan, the oxide reduction peak (0.76 V) is significantly suppressed as well as the hydrogen adsorption processes. The hydrogen desorption is then strongly hindered in the second scan as a consequence of surface blocking species formed during the first scan, however the oxidation process at 0.62 V has not been totally suppressed. As shown later, the oxidation processes occurring in the 0.35–0.90 V potential region are strongly catalyzed by the Pt(1 1 1) surface.

3.2. PVP cyclic voltammetry behavior on Pt(1 1 1)

Fig. 2 presents CV profiles at 50 mV s^{-1} in the 0.05–0.9 V potential range for the Pt(1 1 1) in O_2-free 0.1 M aqueous H_2SO_4 solution in the absence and presence of 1% w/w PVP. In the case of the PVP-free solution (black line), the CV reveals features corresponding to the hydrogen UPD and anion adsorption, and is in total agreement with the form of the curve published by Clavilier and co-workers [14,15], characterizing a clean system and well ordered Pt(1 1 1). It is important to emphasize that experiments with the PVP-containing solution were only carried out after we obtained the typical voltammetric behavior for each single-crystal face in the aqueous H_2SO_4 supporting electrolyte. This procedure assured the electrochemical responses to be solely due to interaction between the Pt surfaces and PVP. Additionally, all the employed single-crystal electrodes were never cycled into the oxide formation/reduction potential region in order to avoid surface reconstruction [16]. Sweeping the potential from 0.05 V to the positive direction, the first CV cycle in the presence of PVP (red line) reveals higher current densities in the hydrogen desorption region (between 0.05 and 0.35 V) than those obtained in the PVP-free solution. At this point is still unclear whether such currents are due to some PVP oxidation or only from hydrogen desorption. The PVP at the interface might have increased the resistance and, consequently, associated higher capacitive currents. In the subsequent cycles (blue and green lines) the current densities in this region are lower and roughly coincidental. As the CV proceeded in the positive direction, the CV transient reveals a broad oxidation wave starting at 0.35 V (centered at about 0.62 V), followed now by a more distinguishable oxidation shoulder at 0.84 V and a lack of features typical for anion adsorption. These anodic currents (between 0.35 and 0.9 V) decreased with cycling, denoting the irreversibility of the process. During the back scan one can see some reactivation (oxidation currents) between 0.35 and 0.9 V, a behavior primarily associated with a partial removal of carbonaceous species that are not completely oxidized in the forward scan. Consequently, free platinum sites are then available for further PVP oxidation. This reactivation broad peak was not observed for the polycrystalline Pt, which suggests a dependence of PVP oxidation on the Pt(1 1 1) orientation. It is later shown that the reactivation is even more pronounced on

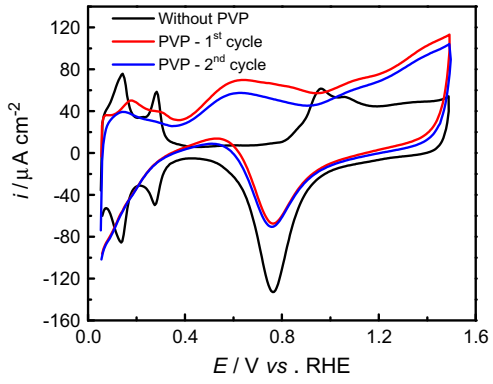

Fig. 1. Cyclic voltammograms for polycrystalline Pt at 50 mV s^{-1} in O_2-free 0.1 M aqueous H_2SO_4 solutions without and with 1% w/w PVP.

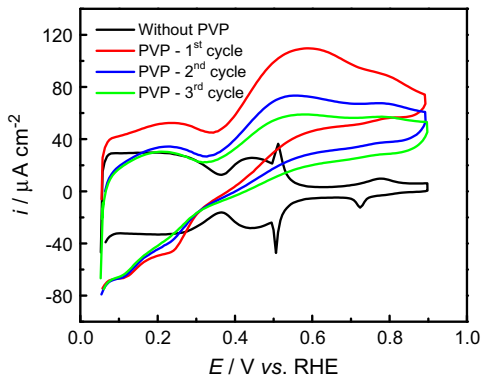

Fig. 2. Cyclic voltammograms for Pt(1 1 1) at 50 mV s^{-1} in O_2-free 0.1 M aqueous H_2SO_4 solutions without and with 1% w/w PVP.

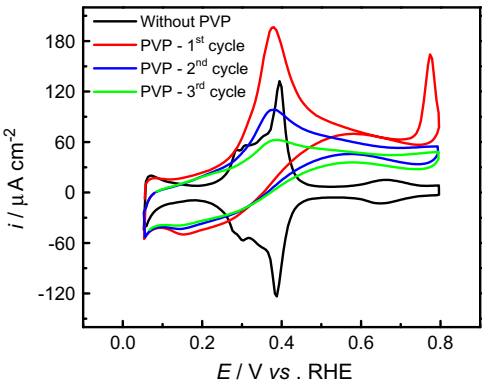

Fig. 3. Cyclic voltammograms for Pt(100) at 50 mV s^{-1} in O_2-free 0.1 M aqueous H_2SO_4 solutions without and with 1% w/w PVP.

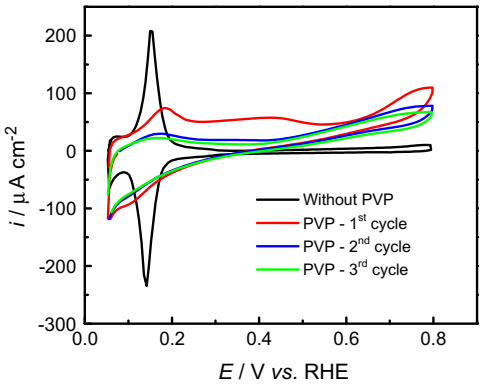

Fig. 4. Cyclic voltammograms for Pt(110) at 50 mV s^{-1} in O_2-free 0.1 M aqueous H_2SO_4 solutions without and with 1% w/w PVP.

Pt(100). The reduction of the oxidation products delivered two reduction peaks in the hydrogen UPD region.

3.3. PVP cyclic voltammetry behavior on Pt(100)

In Fig. 3, we show (CV) profiles obtained at 50 mV s^{-1} in the 0.05–0.8 V potential range for the Pt(100) electrode in O_2-free 0.1 M aqueous H_2SO_4 in the absence and presence of 1% w/w PVP. The black-line CV refers to the 0.1 M aqueous H_2SO_4 and its charge density for hydrogen desorption is 205 μC cm^{-2}. The CV characteristics correspond to the hydrogen UPD and anion adsorption on the Pt(100) electrode and attest that the Pt surface was atomically well-ordered and the system clean [17]. The PVP addition into the 0.1 M aqueous H_2SO_4 drastically changes the CV profile. In the first scan (red line), starting the potential sweep at 0.05 V towards the positive direction, an oxidation process begins at about 0.25 V and develops a peak current at 0.37 V, which is more intense and slightly shifted in comparison to the hydrogen desorption peak (0.39 V) observed in the PVP-free solution. The peak potential remains unchanged upon cycling and its intensity abruptly decreases. These features are surely not only related to the hydrogen/anion processes, but also to some PVP oxidation. The associated charge density in the first CV cycle is 272 μC cm^{-2}, about 32% higher than that obtained in the PVP-free solution. As the hydrogen UPD is limited to one monolayer, the charge excess must have come from PVP oxidation, which is also evidenced by the peak intensity decrease in the subsequent cycles. The charges calculated for the second and third cycles were 90 μC cm^{-2} and 37 μC cm^{-2}, respectively. As the scan progressed, a sharp anodic peak at 0.77 V observed in the first scan completely disappears in the subsequent ones. During the back scan, all CV cycles displayed reactivation. This behavior was less pronounced on the Pt(111) and inexistent on polycrystalline Pt, which suggests strong dependence of PVP oxidation on the Pt(100) orientation. The CV completely lacks the typical hydrogen UPD and anion desorption features and one can observe reduction waves in the 0.32–0.10 V region, being slightly affected with cycling.

3.4. PVP cyclic voltammetry behavior on Pt(110)

Fig. 4 shows a series of CV recorded between 0.05 V and 0.8 V at 50 mV s^{-1} for the Pt(110) in O_2-free 0.1 M aqueous H_2SO_4 in the absence and presence of 1% w/w PVP. In the PVP-free solution

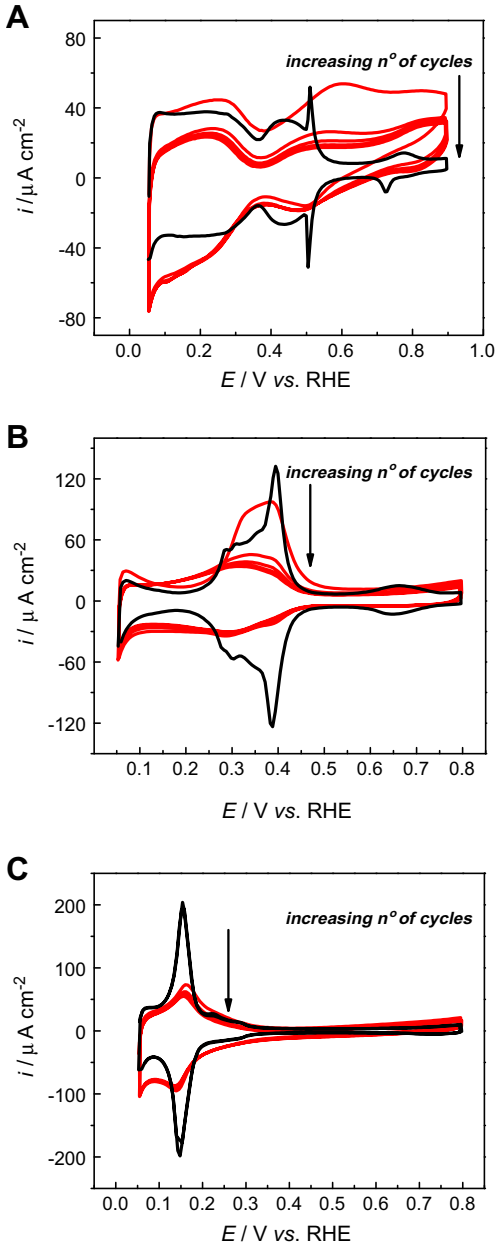

Fig. 5. Series of cyclic voltammograms for PVP-modified single-crystal Pt electrodes recorded at 50 mV s^{-1} in PVP-free 0.1 M aqueous H_2SO_4 solutions: (A) Pt(111), (B) Pt(100) and (C) Pt(110).

(black line) the CV profile depicts symmetric peaks, featuring reversible the hydrogen UPD and anion adsorption processes. Furthermore, the surface was atomically well ordered and the system impurity-free. The integrated-desorption charge gave 214 μC cm^{-2}, which is in good agreement with literature values [9,16]. The addition of 1% w/w PVP into the 0.1 M aqueous H_2SO_4 revealed the following general CV features: (a) three broad asymmetric oxidation waves (asymmetric wave means no correspondent counter part in the cathodic branch of the CV) in the first scan (red line), tending to disappear in the following ones and (b) substantial inhibition of the characteristic hydrogen UPD and anion adsorption/desorption in the first cycle and their complete disappearance in the subsequent ones. The anodic charge density of 14 μC cm^{-2} for the asymmetric broad wave in the 0.05–0.25 V range is substantially smaller than the determined value of 214 μC cm^{-2} in the same potential region. This leads us to the conclusion that the PVP strongly hinders the hydrogen UPD and anion adsorption processes on the Pt(110). With cycling the hydrogen UPD and anion adsorption regions get completely featureless, the broad wave in the 0.25–0.55 V potential range disappears and the anodic process in the 0.55–0.8 V range becomes less intense.

3.5. Effect of adsorbed PVP onto single-crystal Pt

A separate set of experiments was carried out with PVP-modified single-crystal Pt electrodes in order to check the pure effect of PVP adsorption. This was accomplished by immersing just-annealed electrodes in a cell containing 0.1 M H_2SO_4 + 1% w/w PVP at OCP for 2 min, thoroughly rinsing them with ultrapure water and then recording CV transients in a cell containing only 0.1 M H_2SO_4 in their respective potential ranges. The results are displayed in Fig. 5. The CV characteristics are in general the same of those obtained in PVP-containing solutions, however the current densities associated with PVP oxidation are rather lower. This means that, in the case of PVP-containing solutions, some bulk PVP is able to reach the partially blocked electrode surface and undergoes oxidation. It is interesting to note that for the Pt(111) (Fig. 5A) and Pt(100) (Fig. 5B) surfaces the characteristic hydrogen UPD/anion adsorption/desorption processes get more and more featureless with cycling. In the case of Pt(110) (Fig. 5C) such processes are also suppressed, however the current densities remain practically coincidental with cycling. This leads us to conclude that PVP irreversibly adsorbs on all single-crystal surfaces, with Pt(111) and Pt(100) being the most active for its oxidation. Oxidation products may in turn adsorb on Pt(111) and Pt(100) (atomically denser surfaces) and gradually consume active sites for hydrogen UPD/anion adsorption/desorption. Comparison of Fig. 4 with Fig. 5C shows that oxidation current densities in the 0.25–0.8 V range appear for Pt(110) only when PVP is in solution. In its absence no oxidation was probed and therefore the number of sites for hydrogen UPD/anion adsorption/desorption remained roughly constant.

4. Conclusions

In this work we examined the electrochemical behavior of PVP on polycrystalline Pt, Pt(111), Pt(100) and Pt(110). PVP inhibits the characteristic hydrogen UPD and anion adsorption on all investigated surfaces. A variety of oxidation processes were observed upon potential increase on all Pt surfaces, with the Pt(111) and Pt(100) being the most active and giving rise to a reactivation CV broad oxidation peak in PVP-containing solutions. From these results we conclude that the electrochemical behavior of PVP in aqueous H_2SO_4 is strongly dependent on the surface geometry. Experiments with PVP-modified Pt electrodes in PVP-free solutions revealed that PVP irreversibly adsorbs on all investigated surfaces, with the Pt(110) being practically inactive for its oxidation. PVP has been widely used as stabilizing agent in the nanoparticle production field and is usually considered inert. We showed here that this polymer is inert in a narrow potential range, suffering oxidation at potentials higher than 0.4 V *vs* RHE. The oxidation products surely adsorb onto the Pt surface. In our opinion, this fact should be taken into consideration as a protective mechanism by PVP.

Acknowledgments

The authors thank FAPESP, CNPq and CAPES for the financial support.

References

[1] B.S. Yin, H.Y. Ma, S.Y. Wang, S.H. Chen, J. Phys. Chem. B 107 (2003) 8898–8904.
[2] H.Y. Ma, B.S. Yin, S.Y. Wang, Y.L. Jiao, W. Pan, S.X. Huang, S.H. Chen, F.J. Meng, ChemPhysChem 5 (2004) 68–75.
[3] W. Pan, X.K. Zhang, H.Y. Ma, J.T. Zhang, J. Phys. Chem. C 112 (2008) 2456–2461.
[4] S.I. Hsiu, I.W. Sun, J. Appl. Electrochem. 34 (2004) 1057–1063.
[5] P.S. Roy, J. Bagchi, S.K. Bhattacharya, Colloid Surf. A: Physicochem. Eng. Asp 359 (2010) 45–52.
[6] S. Roy, J. Appl. Polym. Sci. 110 (2008) 2693–2697.
[7] S. Clemenson, L. David, E. Espuche, J. Polym. Sci., Part A: Polym. Chem. 45 (2007) 2657–2672.
[8] L.H.S. Gasparotto, J.F. Gomes, G. Tremiliosi-Filho, Electrochem. Solid-State Lett. 14 (2011) P25.
[9] M. DeBlois, J. Lessard, G. Jerkiewicz, Electrochim. Acta 50 (2005) 3517–3523.
[10] M. Rodriguez-Lopez, J. Solla-Gullon, E. Herrero, P. Tunon, J.M. Feliu, A. Aldaz, A. Carrasquillo, J. Am. Chem. Soc. 132 (2010) 2233–2242.
[11] J. Clavilier, K. Elachi, M. Petit, A. Rodes, M.A. Zamakhchari, J. Electroanal. Chem. 295 (1990) 333–356.
[12] F. Hassouna, S. Therias, G. Mailhot, J.-L. Gardette, Polym. Degrad. Stab. 94 (2009) 2257–2266.
[13] J.F. Gomes, B. Busson, A. Tadjeddine, G. Tremiliosi-Filho, Electrochim. Acta 53 (2008) 6899–6905.
[14] J. Clavilier, K. Elachi, A. Rodes, Chem. Phys. 141 (1990) 1–14.
[15] D. Armand, J. Clavilier, J. Electroanal. Chem. 270 (1989) 331–347.
[16] S. Morin, B.E. Conway, J. Electroanal. Chem. 376 (1994) 135–150.
[17] A. Zolfaghari, G. Jerkiewicz, J. Electroanal. Chem. 467 (1999) 177–185.